

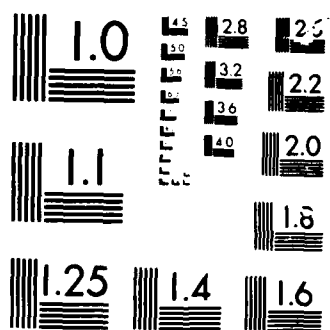
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THE DISCRETE SITE STICKY WALL MODEL(U) PUERTO RICO UNIV 1/1  
RIO PIEDRAS DEPT OF PHYSICS J P BADIALI ET AL.  
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THE DISCRETE SITE STICKY WALL MODEL

by

J.P. Badiali  
Laboratoire Propre No 15 de CNRS  
Physique des Liquides et Electrochimie  
Tour 22, 5e Etage, 4 Place Jussieu  
75230 Paris Cedx 05, France

L. Blum  
Physics Department  
College of Natural Sciences  
P.O. Box AT, Rio Piedras, Puerto Rico 00931

M.L. Rosinberg  
Laboratoire Propre No. 15 de CNRS  
Physique des Liquides et Electrochimie  
Tour 22, 5e Etage, 4 Place Jussieu  
75230 Paris Cedx 05, France

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J.P.Badiali

Laboratoire Propre N°15 de  
Physique des Liquides et Elec  
Tour 22, 5e Etage, 4 Place  
75230 Paris Cedx 05, Fr

*M. Rosinberg, ERDA  
ONR  
Reports  
Send  
To small list*

L.Blum

Physics Department

College of Natural Sciences

POBox AT, Rio Piedras, Puerto Rico 00931

M.L.Rosinberg

Laboratoire Propre N°15 de CNRS  
Physique des Liquides et Electrochimie  
Tour 22, 5e Etage, 4 Place Jussieu  
75230 Paris Cedx 05, France

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## ABSTRACT

The interface between a solid and a liquid is modelled by a flat surface with an array of sticky sites which could be placed on a regular lattice, or also randomly. It is first shown that the thermodynamics and distribution functions can be expressed entirely in terms of the distribution functions of the system without the sticky sites. Furthermore, the problem of the occupation of the sites (equivalent to the adsorption isotherm), is a lattice problem, which exhibits phase transitions and critical points. A simple application to the interface between a solid and a fluid of hard spheres is discussed.

## INTRODUCTION

Real fluid-solid interfaces have a good deal of structure and therefore are very difficult to treat in Statistical Mechanics. Traditionally, the literature has dealt with the structure of the solid side, and therefore, ignored the liquid, or else, treated the liquid using accurate integral equations, but assuming that the surface is perfectly smooth. In the present work we discuss a model of the interface in which the fluid is treated using an integral equation, but instead of a smooth interface, we have an array of sticky sites which represent the atoms in the solid side of the interface. This model is still tractable, and incorporates the surface structure and its effects into the theory. In previous work [1] an exact solution of this model for the 2-dimensional one component plasma was presented.

The model of Langmuir [2] was perhaps the first model of this kind

but in which the fluid was treated as an ideal gas. Further treatments incorporated the structure of the surface as a perturbation [3,4]. The adsorption on a uniformly sticky surface was discussed in the pioneering work of Perram and Smith [5]. In our model, the sticky potential of Baxter  $u_s(r)$  [6] is used. Consider for simplicity a fluid of spheres with a hard core of diameter  $\sigma$  and density  $\rho$  near the wall. The position of the center of the sphere  $\underline{r}=(x,y,z)$ , where  $z$  is the distance to the surface, and  $\underline{R}=(x,y)$  is the position of the projection of the surface. The sticky interaction is then given by

$$\exp[-\beta u_s(r)] = 1 + \lambda(R) \delta(z - \sigma/2) \quad (1)$$

where  $\lambda(R)$  is the stickiness parameter, which could be an arbitrary function of  $R$ . In most cases it will be periodic, and in the case in which the adsorption sites are points we have

$$\lambda(R) = \lambda \sum_{n_1, n_2} \delta(R - n_1 a_1 - n_2 a_2) \quad (2)$$

where  $n_1, n_2$  are natural numbers and  $a_1, a_2$  are the lattice vectors of the sites on the surface.

Consider now a fluid of  $N$  particles in a container of volume  $V$ . The Hamiltonian of the system is

$$H = H^0 + H_a \quad (3)$$

where  $H^0$  is the Hamiltonian in the absence of the sticky interactions

and the sticky interactions are

$$H_a = \sum_i u_a(\underline{r}_i) \quad (4)$$

where the sum is over all sites of the surface. The canonical partition function is

$$Z_N = (1/N!) \int \exp[-\beta H^0] \prod_{i=1}^N ([1 + \lambda(R_i) \delta(z_i - \sigma/2)] d\underline{r}_i) \quad (5)$$

and after some simple manipulations we get [1]

$$Z_N = Z^0 \sum_{s=0}^N (\lambda^s / s!) \rho_s^0(R_1 \dots R_s) \quad (6)$$

all sites  
on the surface

where we have used the definition of the n-particle distribution function

$$\rho_s^0(1 \dots s) = 1/(N-s)! Z^0 \int d\underline{r}_{s+1} \dots d\underline{r}_N \exp[-\beta H^0] \quad (7)$$

$$\rho_s^0(1 \dots s) = \prod_{i=1}^s \rho^0(i) g_s(1 \dots s) \quad (8)$$



It is clear from (5) that  $\lambda$  can be identified, up to a multiplicative constant with the fugacity of the adsorbed particles. The average number of adsorption sites  $\langle N_a \rangle$  is given by

$$\langle N_a \rangle = \partial \ln Z / \partial \ln \lambda \quad (9)$$

Now, the fraction of occupied sites is  $\theta = N_a / M$  where  $M$  is the number of sites in the area  $A$  of the interface. The number of occupied sites per unit area is

$$n_a = \langle N_a \rangle / A = \theta w \quad (10)$$

where  $w = M/A$  is the number of sites per unit area.

The important observation is that the partition function (6) is isomorphic to the grand canonical partition function of a lattice with sites distributed on the surface in the same positions as the sticky sites of our model. The interactions amongst the particles on the sites are obtained by introducing the potentials of mean force of the smooth wall problem (SWP) [7]

$$g_s^c(1 \dots s) = \exp(-\beta [\sum_{\langle ij \rangle} w(i,j) + \sum_{\langle ijk \rangle} w(ijk) + \sum_{\langle ijkl \rangle} w(ijkl) + \dots]) \quad (11)$$

where the potentials of mean force  $w(ij), w(ijk), \dots$  are defined in terms of the SWP interactions. The indices  $i, j, k$ , refer now to the sites on the surface. Furthermore the 'external field' in the mapping is given by

$$\beta B u = - \log [\lambda \rho^0(R)] \quad (12)$$

where  $\rho^0(R)$  is the density at a given site  $R$  on the surface.

We will be concerned with the occupation number of the sites on the surface. There are many different systems of physical interest that can be studied, but for the sake of simplicity, we will first assume that the adsorbate molecules of the fluid are smaller than the site separation. That means that one molecule cannot occupy two sites at the same time, and therefore our problem can be mapped into an Ising problem with arbitrary interactions amongst the lattice points, and in an external field. Further simplification is achieved by assuming that there are only pair interactions, and furthermore, we may restrict ourselves to only nearest neighbor interactions. In this case a simple adsorption isotherm can be obtained from the Bragg-Williams mean field approximation [8]

$$\theta = \frac{\lambda \rho^o(0) [g(\sigma)]^{v \theta/2}}{1 + \lambda \rho^o(0) [g(\sigma)]^{v \theta/2}} \quad (13)$$

where  $\rho^o(0)$  is the wall contact probability of the SWP, and  $g(\sigma)$  is the contact value of the pair distribution function for the fluid, and  $v$  is the number of next nearest neighbors of the lattice.

In terms of the Ising field  $B$ , magnetic moment  $\mu$ , and interaction parameter  $w$  we have

$$\lambda \rho^o(0) = \exp[-\beta B \mu] \quad (14)$$

$$g(\sigma) = \exp[-\beta w] \quad (15)$$

Consider now the case in which a hard sphere fluid is in contact with the [111] face of an closed packed (hexagonal or face centered cubic) crystal of spherical atoms of exactly the same diameter as those of the fluid. This is the case in which the adsorbate is commensurate with the adsorbing surface. Then, we have explicit expressions for both these quantities [9,10]

$$\rho(0) = \rho(1+2\eta)/(1-\eta)^2 \quad (16)$$

$$g(\sigma) = (1+\eta/2)^2/(1-\eta)^4 \quad (17)$$

$$\eta = \frac{\pi}{6} \rho \sigma^3$$

Replacing these expressions into (13) we get

$$\theta = \frac{\lambda \rho(1+2\eta)/(1-\eta)^2 [(1+\eta/2)/(1-\eta)^2]^{v\theta}}{1 + \lambda \rho(1+2\eta)/(1-\eta)^2 [(1+\eta/2)/(1-\eta)^2]^{v\theta}} \quad (18)$$

Figure 1 shows the dependence of the fraction of occupied sites  $\theta$  with the bulk density  $\rho$  for various values of the stickiness  $\lambda$ . For low values of  $\lambda$  it is clear that there is a high degree of cooperativity in the adsorption, since, at a given bulk density  $\rho$ , the fraction of occupied sites  $\theta$  changes suddenly, just as the magnetization of the Ising model for a given value of the applied magnetic field. For high values of the parameter  $\lambda$  this discontinuity disappears, and the isotherm has more the aspect of the original Langmuir isotherm. In fact, for low densities we get

$$\theta = \lambda \rho (1+4\eta) / [1 + \lambda \rho (1+4\eta)]$$

(19)

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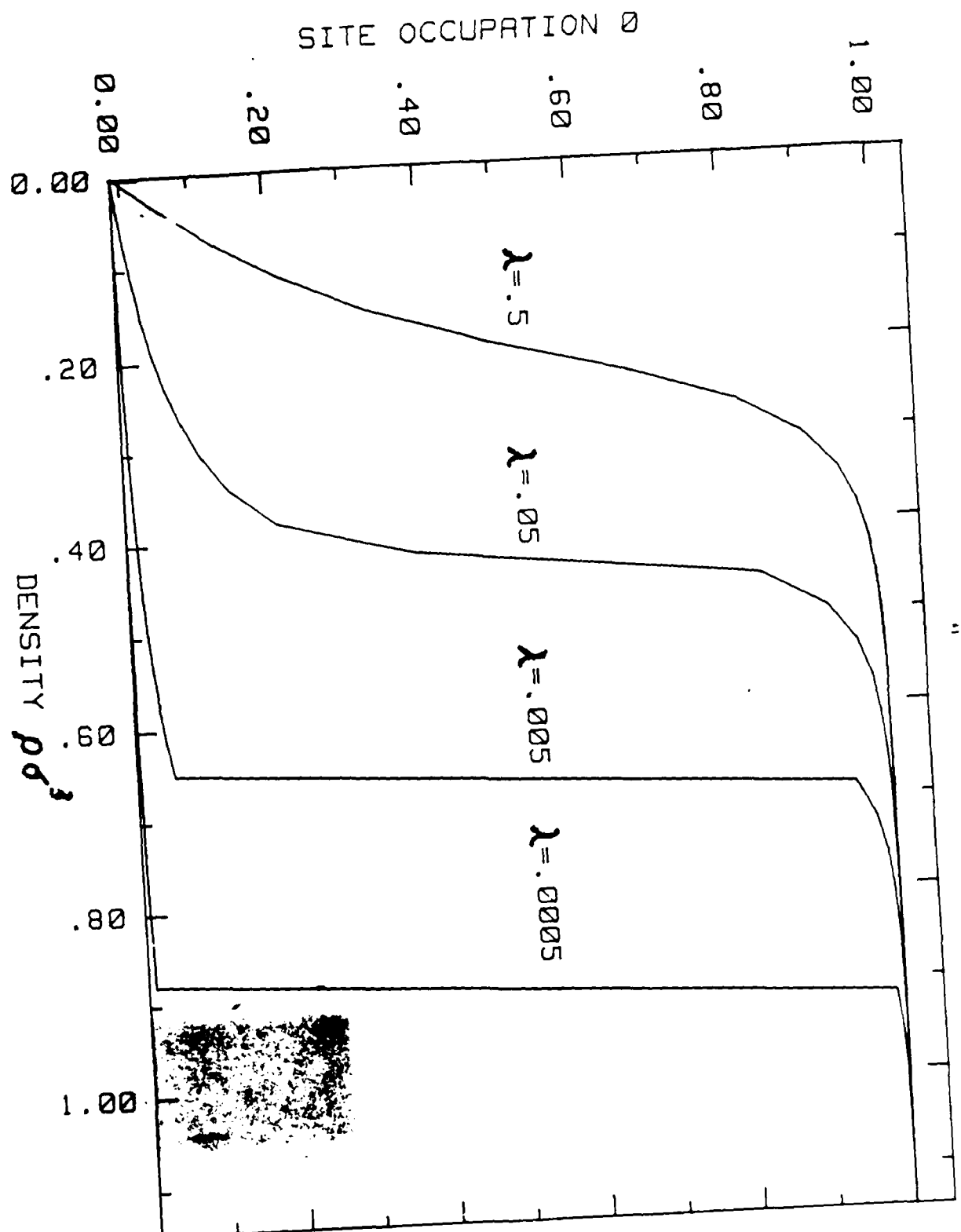


Figure Caption:

Fraction of sites occupied as a function of the reduced density  $\rho\sigma^3$   
for different values of the stickyness  $\lambda$

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